

## **Mechanoluminescence Studies of Gamma Irradiated Sodium Chloride Single Crystals and Microcrystalline Powder Doped with Terbium**

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### **ABSTRACT**

This paper reports the mechanoluminescence (ML) induced by impulsive excitation of  $\gamma$  - irradiated terbium doped NaCl single crystals and powder. The NaCl crystals having different concentrations of terbium were prepared by melt technique (slow cooling). The crystals of small sizes were cleaved from grown crystal block and crushed to obtain powder or microcrystalline powder. The annealed samples were irradiated by gamma source with dose rate of 0.50kGy/hrs. Mechanoluminescence is excited impulsively by dropping a load of 0.4 kg with impact velocity 313 cm/Sec on to it. Two peaks are observed in the ML intensity versus time curves for both single crystals and powder samples. In the ML spectra a broad band with single peak at 539 nm is obtained due to transition of Tb ions from  $^5D_4 \rightarrow ^7F_5$  transitions. The ML intensity of powder sample is less as compared to crystal sample of same mass. The ML intensity of microcrystalline powder increases with particle size.

**Keywords:** Mechanoluminescence, Thermoluminescence,  $\gamma$ -irradiation.

## INTRODUCTION

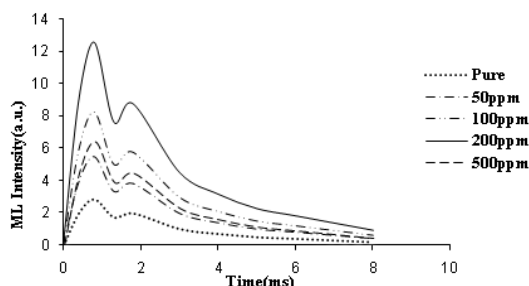
Radiation causes excitation of molecules besides formation of free radicals. The presence of excited states can be discovered by measuring of light emission when crystallite material is heated (thermoluminescence), or stimulated by light (photoluminescence), or when dissolved in suitable solvent (lyoluminescence). Mechanoluminescence is an interesting luminescence phenomenon whereby light emission in solids is caused by mechanical stimuli such as compressing, stretching, fracture, cutting, cleaving, breaking, grinding, rubbing, scratching, and crushing and so on.<sup>1-3</sup> In the recent past, intense ML materials have been prepared whose ML emission can be seen in daylight with naked eye and such materials are finding important applications in novel self-diagnosis systems, optical stress sensors, stress imaging devices<sup>4-6</sup>, wireless fracture sensor systems<sup>7-9</sup> and in damage sensors<sup>10-12</sup>. These materials also find application in fuse system for army warheads<sup>13</sup>. Study of luminescence of rare earth ions is very important as it finds applications in colour television, fluorescent tubes, X-ray phosphors, display panels, security printing and have potential applications in lasers and bio imaging<sup>14</sup>. To enhance the luminescent characteristics of phosphors, extensive research has been carried out on rare earth activated phosphors. Some ML materials have been made to visualize the stress distribution in solids and visualization of stress near the tip of a crack<sup>15-16</sup>. It has been reported that X or  $\gamma$ -irradiated alkali halide crystals<sup>17-19</sup>, Mn-doped zinc sulphide<sup>19-21</sup> and a few polymers<sup>22</sup> show ML when they are deformed elastically. Thermoluminescence

of single crystals and microcrystalline powder of alkali halides have been studied by various research groups<sup>23-28</sup>. Recently Bangaru and Muralidharan (2009, 2010, 2011 & 2012) and Bhujbal *et al.* (2012) also reported the enhanced luminescent properties and thermoluminescence studies in alkali halides by doping rare earth materials<sup>29-35</sup>. The present paper reports ML of gamma irradiated Tb doped NaCl single crystals and microcrystalline powder.

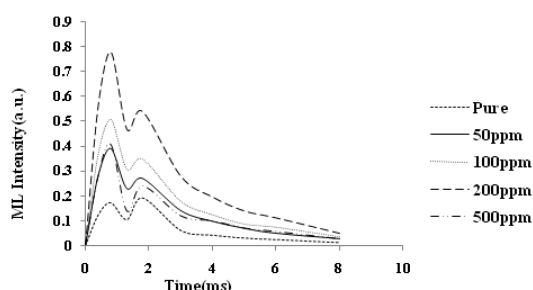
## EXPERIMENTAL

Single crystals of NaCl doped with different concentrations of Tb were grown by melt method. Analar grade chemicals were used in the present investigation. The crystals of small sizes were cleaved from the grown crystal blocks. To obtain powder of the sample it was crushed and sieved. The crystals so grown and the microcrystalline powder of different sizes (75- 180 $\mu$ m) as obtained were annealed at 450<sup>0</sup>C for two and half hours and subsequently cooled to room temperature. The irradiation of samples was carried out using <sup>60</sup>Co gamma source having exposure rate of 0.50 kGy/hour. The ML was excited impulsively by dropping a load of mass 0.4 kg on to the gamma-irradiated sample placed on the Lucite plate from the height of 50 cm using a guiding cylinder. The impact velocity of the load is determined by the relation  $v = \sqrt{2gh}$ . The ML was monitored by RCA 931 photomultiplier tube positioned below the Lucite plate and connected to storage oscilloscope (Sciencific SM-340). ML emission was recorded by inserting filters of different wavelength between lucite plate and photomultiplier tube.

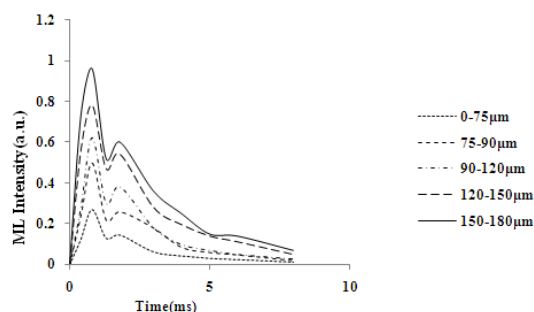
## Results and discussion



**Fig 1: Time Dependence of ML Intensity of NaCl: Tb Single crystals. (0.25kGy)**



**Fig 2: Time Dependence of ML Intensity of NaCl: Tb powder (120-150µm). (0.25kGy)**



**Fig 3: Mechanoluminescence glow curve of Tb doped NaCl microcrystalline powder (200ppm) (0.25kGy)**

Figures 1 shows time dependence of ML intensity of gamma irradiated NaCl single crystals and powder doped with different concentration of Tb. Where, two

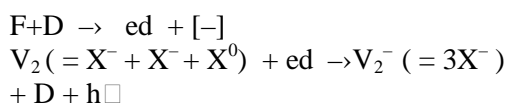
peaks are observed in the ML intensity versus time curve. The ML intensity of first and second peak as well as total ML intensity increases with increasing concentration of dopant up to 200ppm without any considerable change in  $t_m$  i.e. time corresponding to ML peaks. Thereafter the ML intensity decreases with further increase in concentration of dopant. Similar results are observed for NaCl: Tb powder samples (Fig. 2); however the ML intensity of powder sample (120-150µm) is less as compared with crystal sample. The results were taken for known quantity of microcrystalline powder (of the same mass).

Figure 3 represents the dependence of ML intensities of NaCl: Tb (200ppm) microcrystalline powder of various sizes. The intensities of microcrystalline powder increase with size.

This is because, when alkali halide crystal is exposed to high energy radiation like  $\gamma$ -rays or x-rays, excitation of electrons of halides atoms from valence band to conduction band takes place. Some of the excited electrons return immediately from the conduction band to the valence band; however some of the electrons in the conduction band get trapped in the negative ion vacancies during their movement and consequently the formation of colour centers takes place. Initially the number of colour centers increases with the radiation doses given to the crystals and thereby, the ML intensity increases with the radiation dose. However for long duration of the irradiation of the crystals the recombination between electrons and holes takes place and consequently the density of colour centres in the crystals attains a saturation value. As a matter of fact, the luminescence intensity

attains a saturation value for high radiation doses given to the crystallites<sup>36</sup>.

In alkali halide crystals, the electron dislocation band lies just above the F-centre level where the energy gap between the bottom of the dislocation band and ground state of an F-centre is of the order of 0.10 eV<sup>37, 38</sup>. Near an edge dislocation, some of F-centres lie in the compression region and some of them lie in the expansion region. As the energy gap between two levels in alkali halide crystals decreases with decrease in the local density of crystals, the energy gap between dislocation band and ground state of F-centre may increase in the compression region due to the increase in local density of the crystals. The electrons captured by a dislocation have a finite lifetime. If the moving dislocation containing electrons encounters the defect centers containing holes, the dislocation electrons may be captured by these centres and luminescence may arise due to the radiative recombination of electrons from F-centres with the hole in V<sub>2</sub> centres. Schematically, the ML process can be described by the following equations.



where F and D represent the F-centre and dislocation, respectively, *ed* is the dislocation electron i.e. the electron captured by a dislocation, ( - ) is the negative ion vacancy, X<sup>-</sup> is the halogen ion, X<sup>0</sup> is the self trapped hole and V<sub>2</sub><sup>-</sup> is the V<sub>2</sub> centre with captured electron<sup>1,39</sup>. The effect of incorporating rare earth impurities into insulating host crystals during crystal growth involves several considerations which include whether interstitial or substitutional

sites are occupied, the clustering of impurities, possible precipitation of impurities to form new phases and the question of charge compensation of the impurities ions<sup>27</sup>. In the present work doping of Tb<sup>3+</sup> lead to charge compensating vacancies in NaCl, which increases the probability of formation of colour centers. The trivalent impurity ion Tb<sup>3+</sup> enters the crystal replacing Na<sup>+</sup> ions. During γ-irradiation electron hole pairs are created as expected hole is captured by host related centers and some of the released electrons are captured by the impurity Tb<sup>3+</sup> ions reducing these to Tb<sup>2+</sup> ions in addition to the formation of F-centers. So γ -irradiated rare earth doped alkali halide crystals, rare earth ions enhance the relative density of defects. That is why the ML intensity increases with dopant concentration<sup>40</sup>.

It is suggested that ML of NaCl: Tb is strongly related to the movement of dislocations and the recombination of activated electrons and holes. The movement of dislocations excites carriers from the filled traps and the subsequent recombination of the electrons and holes in luminescence centers (Tb<sup>3+</sup>). The first peak which occurs in the deformation region of the phosphors may be attributed to the ML produced due to the charging of newly created surface. However, second ML peak which occurs in the post deformation region may be due to the capture of carriers by the shallow traps lying away from the newly created surfaces where the electric field near the surface is not so effective. The release of trapped carriers from the shallow traps may take place later on due to the thermal vibration of the lattice and therefore, a delayed ML may be produced which may lie

on the post deformation region of the phosphors<sup>41</sup>.

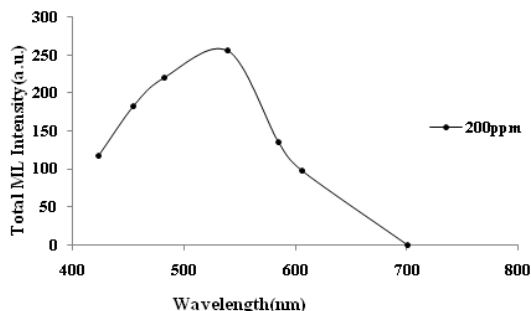


Fig 4: ML Spectra of  $\gamma$ -irradiated NaCl: Tb (200ppm) crystal

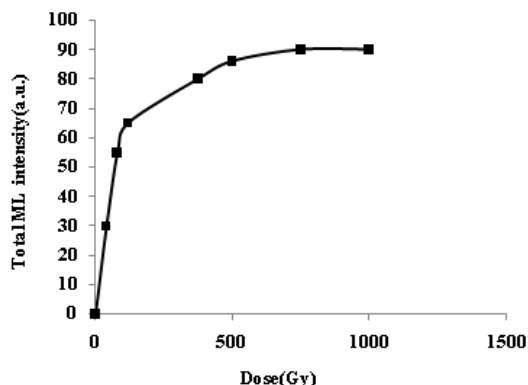


Fig 5: Dependence of ML intensity of  $\gamma$ -irradiated NaCl: Tb (200ppm) crystals on the gamma doses

Figure 4 represents the ML spectra of single crystals of NaCl: Tb. The ML spectra consist of a broad band with single peak at 539 nm for doped crystals. The luminescence efficiency gets enhanced by the incorporation of Tb-ions in the NaCl matrix. It has been reported that the spectrum of a given  $\text{RE}^{3+}$  ion is essentially the same in various host lattices. The major emission in  $\text{Tb}^{3+}$  doped is due to the transition  $^5\text{D}_4 \rightarrow ^7\text{F}_j$  which is mainly in the green region and often there is a

considerable contribution to the emission from the higher-level emission  $^5\text{D}_3 \rightarrow ^7\text{F}_j$ , mainly in the blue region. In the present study we noticed that in the ML spectra of NaCl: Tb, the effect of incorporation of terbium is the overall intensity enhancement in the host emission from 423nm to 580nm takes place with broad peak at 539nm. Which may be obtained due to transition of Tb ions from  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition?

Figure 5 represents the dependence of ML intensities of NaCl: Tb crystals on various doses. It is noticed that the total ML intensity initially increases with increasing irradiation dose, and then attain saturation values around 1000 Gy. Similar results are obtained for microcrystalline powder samples with weak ML intensities (not shown in this paper).

The decrease in ML of microcrystalline powder than single crystal could arise for several reasons. In microcrystalline powder, large number of grosser defects such as dislocations, grain boundaries, etc., will be produced during crushing of single crystals. This will increase the surface to volume ratio of the system. During irradiation the colour centre production may get affected by the presence of this surface and dislocations (defects). This could be the reason for the less luminescence intensity in the small size microcrystalline powder. Lesser stability of the colour centres produced after irradiation in smaller size microcrystalline powder could be the reason for less luminescence intensity. Further the dislocations (defects) may increase the diffusion which leads to increased recombinations which are inefficient to yield good ML intensity. On the other hand these dislocations may also

act as sink for some defects responsible for ML and thus reduce the number of defects and hence the weak ML intensity. Further the adsorbed gases and moisture, on the surface may lead to non-radiative recombinations which in turn reduce the intensity yield in ML of microcrystalline powder. Moreover we may expect that these effects will go on increasing with the decreasing particle size and hence the less ML intensity with decreasing particle size is expected.

## CONCLUSIONS

We have investigated the ML of single crystals and microcrystalline powder of NaCl doped with terbium and we found that two peaks in ML glow curve. The first peak lies in the deformation region and the second peak lies in the post deformation region. The Peak and total ML intensity is dependent on dopant concentration of terbium and gamma ray irradiation doses. The ML intensity of microcrystalline powder increases with particle size. The ML spectra of doped crystals with broad peak at 539 nm signifies the presence and participation of terbium ions in the ML phenomenon. ML emission in the present samples are induced by the gamma ray irradiation and depends on gamma ray doses, and maximum intensity is obtained for low concentration of impurity, which is a good characteristics for the development of materials for radiation dosimeter (costwise) so phosphor NaCl:Tb may be useful in mechanoluminescence dosimeter.

## REFERENCES

1. Chandra B.P., in: D.R. Vij (Ed.), *Luminescence of Solids*, Plenum Press, New York, p. 361 (1998).
2. Molotskii M.I. *Sov. Sci. Rev. Chem.* 13, 1 (1989).
3. Walton A.J., *Adv. Phys.* 26, 887 (1977).
4. Xu C.N., Watanabe T., Akiyama M., Sun P., Zheng X.G. *J. Am. Ceram. Soc.* 82 2342 (1999).  
DOI:10.1111/j.1151-2916.1999.tb02089.x
5. Xu C.N., Watanabe T., Akiyama M., Zheng X.G. *Appl. Phys. Lett.* 74, 1236 (1999).  
DOI: 10.1063/1.123510
6. Xu C.N., Watanabe T., Akiyama M., Nonaka K., Watanabe T. *Appl. Phys. Lett.* 76, 179 (2000).  
DOI: 10.1063/1.125695
7. Xu C.N., Watanabe T., Akiyama M., Sun P., Zheng X.G., in: *Proceedings of the Sixth International Symposium on Ceramic Materials and Composites for Engines, Arita, Japan*, p. 937 (1997).
8. Akiyama M., Xu C.N., Nonaka K., Watanabe T., *Appl. Phys. Lett.* 73, 3046. (1998).  
DOI: 10.1063/1.122667
9. Akiyama M., Xu C.N., Matsui H., Nonaka K., Watanabe T. *Appl. Phys. Lett.* 75, 2548.  
DOI: 10.1063/1.125073
10. Sage I., Badcock R., Humberstone L., Geddes N., Kemp M., Bourhill G. *Smart Mater. Struct.* 8, 504 (1999).  
DOI: 10.1088/0964-1726/8/4/308
11. Sage I., Humberstone L., Oswald I., Lloyd P., Bourhill G. *Smart Mater. Struct.* 10 (2), 332 (2001).  
DOI: 10.1088/0964-1726/10/2/320

12. Sage I., Bourhill G. *J. Mater. Chem.*, 11, 231 (2001).  
DOI: 10.1039/B007029G
13. Dante J.G., Report by Secretary of the Army, USA, (1983).
14. Atabaev, T. S., Hwang, Yoon-Hwae. and Kim, Hyung-Kook. *Nanoscale Research Letters*, 7,556 (2012).
15. Chao-Nan Xu, Xu-Guang Zheng, Morito Akiyama, Kazuhiro Nonaka, *Appl. Phys. Lett.* 76, 179 (2000).  
DOI: 10.1063/1.125695
16. C. Li, Xu C. N., Zhang L., Yamada H., Imai Y. *Journal of Visualization*, Volume 11, Issue 4, 329-335 (2008).  
DOI: 10.1007/BF03182201
17. Shmurak S.Z., Eliasberg M.B. *Sov. Phys. Sol. State* 9, 1427 (1967).
18. Chandra B.P., Bisen D.P. *Phys. Stat. Sol. (a)*, 132, K101 (1992).  
DOI: 10.1002/pssa.2211320237
19. Alzetta G., Chudacek I., Scarmozzino R. *Phys. Stat. Sol. (a)* 1,775 (1970).  
DOI: 10.1002/pssa.19700010417
20. Alzetta G., Minnaja N., Santucci S. *Nuovo Cimento*. 23, 910 (1962).
21. Meyer K., Obrikat D., Rossberg D. *Kristall U. Tech.* 5, 5 (1970).
22. Reynolds G.T., Ausin R.H. *J. Lumin.*, 92, 79 (2000).  
DOI: 10.1016/S0022-2313(00)00230-1
23. Ausin V. and Alvarez-Rivas J L. *Phys. Rev. B* 6 4828 (1972).
24. Patley S. M., Moharil S. V. and Deshmukh B. T. *J. Phys.: Condens. Matter* 1, 2537-2544 (1989).  
DOI: 10.1088/0953-8984/1/14/009
25. Sastry S. B. S. *Nuclear Tracks*, Vol.10, Nos.1/2, 9-20 (1985).
26. Davidson, A. T., Kozakiewicz, A. G., Derry, T. E., Comins, J. D., Suszynska, M. *Radiation Effects and Defects in Solids*, Volume 157, Issue 6-12 629-636 (2002).  
DOI: 10.1080/10420150215750
27. Davidson, A. T., Kozakiewicz, A. G., Derry, T. E., Comins, J. D., and Suszynska, M. *Nuclear Instruments and Methods in Physics B*.218, 249-254 (2004).  
DOI: 10.1016/j.nimb.2004.01.01
28. Davidson A.T., Valberg L., Townsend P.D., Kozakiewicz A.G., Derry T.E., Comins J. D., Suszynska M. *Nuclear Instruments and Methods in Physics Research B*, 250, 354–358 (2006).  
DOI: 10.1016/j.nimb.2006.04.137
29. Bangaru, S., Muralidharan, G., *J. Lumin.* 129, 24-29 (2009).  
DOI: 10.1016/j.jlumin.2008.07.011
30. Bangaru, S., Muralidharan G., Brahmanandhan G.M., *J. Lumin.* 130, 618-622 (2010).  
DOI: 10.1016/j.jlumin.2009.11.005
31. Bangaru, S. *Physica B: Condensed Matter*. 406,159-164 (2011).  
DOI: 10.1016/j.physb.2010.10.022,
32. Bangaru, S., Muralidharan G. *Physica B*, Volume 407, Issue 12, 2185-2189 (2012).  
DOI: 10.1016/j.physb.2012.02.038
33. Bhujbal, P. M. and Dhoble, S. J. *Radiation Effects & Defects in Solids.*, Vol. 167, No. 6, 428–435 (2012).  
DOI: 10.1080/10420150.2011.620957
34. Bhujbal, P. M. and Dhoble, S. J. *Indian J. Phys.*, 86(5): 383–386 (May 2012).  
DOI: 10.1007/s12648-012-0046-x
35. Bhujbal, P. M. and Dhoble, S. J., *Indian J. of Pure & Applied Physics*. Vol.50, 34-37 (2012).
36. Chandra, B. P., Tiwari, R. K., Mor, R., Bisen, D. P. *J. Lumin.*, 75, 127 (1997).
37. Molotskii, M. I., Shmurak, S. Z. *Phys. Stat. Sol. (a)* 120, 83 (1990).

38. Hagihara, T., Hayashiuchi, Y., Yamamota, Y., Ohwakli, S., Okada, T. *Phys. Lett*, A137, 213 (1989).
39. Chandra, B. P., *Radiation Effects and Defects in Solids*, Vol.138, 119 (1996).
40. Johnson, P. D., Williams, F. E. *J. Chem. Phys.*, 18, 1477 (1950).
41. Chandra B. P., Ramrakhiani M., *Phys. Stat. Sol. (a)*, 134, 529 (1992).